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Final Technical Report
(AFOSR Grant No. F49620-92-J-0011)

**THEORETICAL STUDIES OF FUNDAMENTAL PROCESSES IN
SILICON AND DIAMOND CVD AND OTHER SYSTEMS**

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Abstract

The research progress for AFOSR grant F49620-92-J-0011 for the period 1 November 1991 to 31 October 1995 is described. Three main areas of research are described: Chemical vapor deposition (CVD) processes, chemistry in rare-gas matrices, and statistical versus nonstatistical effects in unimolecular reactions. A wide range of studies were performed using classical trajectory methods, Monte Carlo transition-state theory, and *ab initio* quantum mechanical calculations.

I. Publications

All of the significant work accomplished is readily accessible in published form. The following is a list of the publications that results from the work performed with support from AFOSR grant F49620-92-J-0011.

B. W. Spath and L. M. Raff, "*Phenomenological and Monte Carlo Modes for Diffusion-Controlled Bimolecular Reactions in Matrices,*" J. Phys. Chem. **96**, 2179 (1992).

J. Peploski, D. L. Thompson, and L. M. Raff, "*Molecular Dynamics Studies of Elementary Surface Reactions of C_2H_2 and C_2H in Low-Pressure Diamond-Film Formation,*" J. Phys. Chem. **96**, 8538 (1992).

X. Y. Chang, T. D. Sewell, L. M. Raff, and D. L. Thompson, "*Power Spectra as a Diagnostic Tool in Probing Statistical/Nonstatistical Behavior in Unimolecular Reactions,*" J. Chem. Phys. **97**, 7354 (1992).

L. M. Raff, "*Effects of Lattice Morphology Upon Reaction Dynamics in Matrix-Isolated Systems,*" J. Chem. Phys. **97**, 7459 (1992).

X. Y. Chang, D. L. Thompson, and L. M. Raff, "*Intramolecular Energy Transfer Rates Using Fourier Transform Methods,*" Chem. Phys. Letters **206**, 137 (1993).

X. Y. Chang, M. Perry, J. Peploski, D. L. Thompson, and L. M. Raff, "*Theoretical Studies of Hydrogen-Abstraction Reactions From Diamond and Diamond-like Surfaces,*" J. Chem. Phys. **99**, 4748 (1993).

X. Y. Chang, D. L. Thompson, and L. M. Raff, "*Minimum-Energy Paths for Elementary Reactions in Low-Pressure Diamond-Film Formation,*" J. Phys. Chem. **97**, 10112 (1993).

M. B. Ford, A. D. Foxworthy, G. J. Mains, and L. M. Raff, "*Theoretical Investigations of O_3 Vibrational Relaxation and Oxygen Atom Diffusion Rates in Ar and Xe Matrices,*" J. Phys. Chem. **97**, 12134 (1993).

X. Y. Chang, D. L. Thompson, and L. M. Raff, "*Hydrogen-Atom Migration on a Diamond (111) Surface,*" J. Chem. Phys. **100**, 1765 (1994).

X. Y. Chang, K. L. Bintz, D. L. Thompson, and L. M. Raff, "*Classical Intramolecular Energy Transfer Rates Using Fourier Transform Methods: Four-Atom Systems,*" J. Phys. Chem. **98**, 6317 (1994).

D. C. Sorescu, D. L. Thompson, and L. M. Raff, "*Diffusion of Hydrogen Atoms on a Si(111)-(7x7) Reconstructed Surface: Monte Carlo Variational Phase-Space Theory,*" J. Chem. Phys. **101**, 1638 (1994).

M. D. Perry and L. M. Raff, "Theoretical Studies of Elementary Chemisorption Reactions on an Activated Diamond(111) Terrace," J. Phys. Chem. **98**, 8128 (1994).

M. D. Perry and L. M. Raff, "Theoretical Studies of Elementary Chemisorption Reactions on an Activated Diamond Ledge Surface," J. Phys. Chem. **98**, 4375 (1994).

D. C. Sorescu, D. L. Thompson, and L. M. Raff, "Statistical Effects in the Skeletal Inversion of Bicyclo[2.1.0]pentane," J. Chem. Phys. **101**, 3729 (1994).

P. M. Agrawal, D. L. Thompson, and L. M. Raff, "Theoretical Investigation of Nonstatistical Dynamics, Energy Transfer and Intramolecular Vibrational Relaxation in Isomerization Reactions of Matrix-Isolated HONO/Xe," J. Chem. Phys. **99**, 9937 (1994).

P. M. Agrawal, D. L. Thompson, and L. M. Raff, "Theoretical Studies of the Effects of Matrix Composition, Lattice Temperature and Isotopic Substitution on Isomerization Reactions of Matrix-Isolated HONO/Ar," J. Chem. Phys. **102**, 7000 (1995).

D. C. Sorescu, D. L. Thompson, and L. M. Raff, "Molecular Dynamics Studies of the Thermal Decomposition of 2,3-Diazabicyclo(2.2.1)hept-2-ene," J. Chem. Phys. **102**, 7910 (1995).

D. C. Sorescu, D. L. Thompson, and L. M. Raff, "Statistical Effects in the Thermal Deazetization Reaction of 2,3-Diazabicyclo(2.2.1)hept-2-ene," J. Chem. Phys. **103**, 5387 (1995).

II. Major Accomplishments

Since the research that was completed in this project has been published in the open literature and is thus readily accessible, we give only a brief description of the major accomplishments of the work performed. There are three main areas of focus of the research: Statistical versus nonstatistical effects in unimolecular reactions, chemistry in rare-gas matrices, and chemical vapor deposition (CVD) processes.

A. Statistical versus nonstatistical effects in unimolecular reactions

Studies by Sewell and Thompson [T. D. Sewell and D. L. Thompson, *J. Chem. Phys.* **93**, 4077 (1990)] show that the microcanonical dissociation rates are insensitive to the initial partitioning of energy in the 2-chloroethyl radical. On the other hand, in bond fission reactions of Si_2H_6 and 1,2-difluoroethane there is significant mode-selectivity. The rates are quite sensitive to the initial energy distribution among the vibrational modes [H. W. Schranz, L. M. Raff, and D. L. Thompson, *J. Chem. Phys.* **94**, 4219 (1991); *J. Chem. Phys.* **95**, 106 (1991); *Chem. Phys. Letters* **182**, 455 (1991); P. M. Agrawal, D. L. Thompson, and L. M. Raff, *J. Chem. Phys.* **92**, 1069 (1990); L. M. Raff, *J. Chem. Phys.* **90**, 6313 (1989)]. Thus, we carried a additional study to investigate the statistical and nonstatistical behaviors for these reactions. We have shown that it is not sufficient that the total intramolecular energy transfer rate from a given vibrational mode be fast relative to the unimolecular reaction rate to ensure statistical behavior and non-specificity in the chemistry. We have performed a series of calculations that have led to the formulation of three general principles concerning nonstatistical dynamics: Unimolecular reactions will tend to exhibit nonstatistical dynamics if (1) the total internal energy is close to the dissociation threshold, (2) motion along the reaction coordinate does not produce large energetic changes in one

or more bonds in the remainder of the molecule, and (3) there is a formation coordinate for the activated reactant that is strongly coupled to the dissociation coordinate but only weakly coupled to the other internal coordinates of the molecule. [T. D. Sewell, H. W. Schranz, D. L. Thompson, and L. M. Raff, J. Chem. Phys. 95, 8089 (1991).]

We have extended that work by using power spectral analysis. More specifically, we have shown that nonstatistical behavior can be identified by using power spectra provided that the time dependencies of the coordinates are transformed and not the autocorrelation functions of them, and provided that the power spectra are calculated for conditions similar to those leading to reaction. [X. Y. Chang, T. D. Sewell, L. M. Raff, and D. L. Thompson, J. Chem. Phys. 97, 7354 (1992).]

A new method has been developed to obtain mode-to-mode rate coefficients for intramolecular vibrational energy transfer (IVR) from Fourier transforms of the time variation of classical trajectory-determined local-mode bond energies. [X. Y. Chang, D. L. Thompson, and L. M. Raff, 206, 137 (1993); and X. Y. Chang, K. L. Bintz, D. L. Thompson, and L. M. Raff, J. Phys. Chem. 98, 6317 (1994).]

We have investigated statistical (versus nonstatistical) effects in reactions of bicyclo(2.1.0) pentane (BCP) and 2,3-diazabicyclo(2.2.1)hept-2-ene-exo,exo-5,6-d₂ (DBHD) by using classical trajectories. Semiempirical potential energy surfaces were developed by using the available experimental data and by performing *ab initio* calculations. We found that for random energization of the vibrational modes of BCP the dynamics results are in good agreement with the predictions of statistical theory. We also used classical trajectories to study the deazetization reaction in DBHD. Again, we find that statistical predictions agree with our dynamics results. We conclude that the experimentally observed nonstatistical exo/endo product ratio may be due to the post-transition-state dynamics; that is, the system does not have sufficient time to explore all of the available phase space prior to the closure of the 1-3

bridgehead bond. [D. C. Sorescu, D. L. Thompson, and L. M. Raff, J. Chem. Phys. 101, 3729 (1994); 102, 7910, (1995); 103, 5387 (1995).]

B. Chemistry in rare-gas matrices

Phenomenological and Monte Carlo models were developed to describe the kinetics of diffusion-controlled bimolecular reactions in rare-gas matrices. The models are based on the hypothesis that the experimentally observed kinetic behavior is results from inhomogeneity of the matrix and thus the matrix comprises different types of zones, and that there is a characteristic diffusion coefficient or distribution of diffusion coefficients for each of the zones. We showed that the expansion coefficients in a power series representation of the time dependence of the logarithm of the reactant concentration are related in a simple manner to the various number-weighted moments of the diffusion coefficient distribution. [B. W. Spath and L. M. Raff, J. Phys. Chem. 96, 2179 (1992).]

The dynamics of vibrationally excited ozone isolated in Ar and Xe matrices at 12 K were investigated by using classical trajectories. We also developed a new Markov walk/damped trajectory procedure to increase the rate of convergence in a classical variation transition-state theory, and used it to study oxygen-atom diffusion in these matrices. Comparisons of the computed results to experimental data indicates that the measured diffusion coefficients are for diffusion along lattice defects, grain boundaries, vacancies, and other lattice imperfections. [M. B. Ford, A. D. Foxworthy, G. J. Mains, and L. M. Raff, J. Phys. Chem. 97, 12134 (1993).]

We have studied the effects of lattice morphology on the reaction dynamics of *cis*-d₂-ethylene + F₂ in vapor-deposited Ar matrices at 12 K by using classical trajectory methods with nonstatistical sampling to enhance the reaction probabilities. The initial conditions for the trajectories were generated by a combination of Monte

Carlo, damped trajectories, and volume contraction methods. The matrices generated by this procedure are amorphous with numerous vacancies and other imperfections. The calculations show that fluoroethylene elimination results from an atomic addition mechanism in amorphous matrices. This study shows that accurate simulations of matrix-isolation processes require proper descriptions of the matrix corresponding to the experimental conditions; the model must properly represent the lattice structure in the experiment. [L. M. Raff, J. Chem. Phys. 97, 7459 (1992).]

We have carried out molecular dynamics studies of matrix composition, lattice temperature, and isotopic substitution on the *cis-trans* isomerization rates and the vibrational -to-lattice phonon modes energy transfer rates for HONO, DONO, and $\text{H}^{18}\text{ON}^{18}\text{O}$ in Ar and Xe. We found that the *cis-trans* isomerization (in both directions) rates are significantly greater in the matrices than in the gas phase in spite of the steric effects due to the matrix environment. This is because the matrix opens a vibration→lattice-phonon-modes→rotation→torsional-vibration energy transfer route. The calculated rates show significant nonstatistical effects. The IVR rates in the matrix and in the gas phase are slow relative to the isomerization rates, thus isomerization are not statistical. Vibrational relaxation to the lattice is almost independent of the initial energy distribution in the molecule. This may be due to the HONO→lattice energy transfer rates approaching the limiting values determined by the Debye frequency of the lattice. The presence of lattice vacancies exert a profound influence on the dynamics. When the percentage of lattice vacancies approaches 20%, the behavior of the molecule in the matrix approaches that in the gas phase. [P. M. Agrawal, D. L. Thompson, and L. M. Raff, J. Chem. Phys. 101, 9937 (1994); 102, 7000 (1995).]

C. Chemical vapor deposition (CVD) processes

The diffusion of hydrogen atoms on a Si(111)-(7×7) reconstructed surface was studied by using Monte Carlo variational phase-space theory including tunneling effects. The diffusion coefficient was calculated as a function of temperature; the calculated activation energy is in excellent agreement with the experimental value. The study shows that the H-atom diffusion between atop sites of the surface occurs along paths that involve lattice penetration. We find that tunneling effects are small. [D. C. Sorescu, D. L. Thompson, and L. M. Raff, *J. Chem. Phys.* **101**, 1638 (1994).]

Molecular dynamics studies of various reactions involving C_2H_2 and C_2H on various carbon surfaces were done for conditions corresponding to low-pressure diamond-film growth. We find that the chemisorption of C_2H_2 most frequently involves the formation of two $C_{(g)}-C_{(s)}$ bonds to adjacent adsorption sites on the clean C(111) surface. We also observed chemisorption of acetylene by the formation of only C-C bond with the surface with the subsequent desorption of an ethenyl radical, however, this is not a high probability process for the clean C(111) surface. There is a small probability addition of a second C_2H_2 for all the carbon surfaces except clean C(111). When chemisorption of a second molecule does occur, there is a large probability of subsequent desorption of the C_2H_2 unless the ethenyl radical is able to form a C-C bond. Addition of a $\cdot C\equiv CH$ radical to a chemisorbed acetylene group has a much higher probability than is the case for acetylene. The radical is also readily chemisorbed to other surface structures with a low probability of subsequent desorption. Based on the results of this study, ethenyl radical is predicted to be an important diamond-growth species even in experiments in which its concentration is 1 or 2 orders of magnitude less than that of acetylene. [J. Peploski, D. L. Thompson, and L. M. Raff, *J. Phys. Chem.* **96**, 8538 (1992).]

Phenomenological models of diamond-film growth include numerous reactions involving H-atom abstractions, thus we have carried out calculations to study them. Reaction probabilities, cross sections, thermal rate coefficients, frequency factors, and activation energies for H-atom abstraction from a H-covered C(111) surface were computed by using quantum wave packet and classical trajectory methods on an empirical potential energy surface. The computed results suggest that growth models that assume either an equilibrium distribution between surface hydrogen and H₂ or a common abstraction rate for surface H-atoms are unlikely to be accurate. [X. Y. Chang, M. Perry, J. Peploski, D. L. Thompson, and L. M. Raff, J. Chem. Phys. 99, 4748 (1993).]

In a subsequent, related, brief study we showed that hydrogen migration between adsorption sites on a clean C(111) surface is significantly slower than between various chemisorbed moieties that might reasonably be formed during diamond-film formation. [X. Y. Chang, D. L. Thompson, and L. M. Raff, J. Chem. Phys. 100, 1765 (1994).]

We have determined the minimum-energy paths on the Brenner empirical hydrocarbon potential [D. W. Brenner, Phys. Rev. B42, 9458 (1990)] for various reactions including H-atom abstraction and migration, acetylene, ethenyl radical, and H-atom addition to a carbon radical site, and 6-membered, carbon-ring closure. The barrier to addition of C₂H₂ or C₂H via C_s-C single-bond formation at some radical site is within the range of thermal energies. Ring closures between two radical sites are near barrierless processes. The results indicate that H-atom abstraction is very likely the rate-determining step in low-pressure, diamond-film growth. [X. Y. Chang, D. L. Thompson, and L. M. Raff, J. Phys. Chem. 97, 10112 (1993).]

The chemisorption and reaction dynamics on an activated diamond (111) terrace and ledge structures have been studied for H, C₂H₂, C₂H, CH₃, CH₂, C₂H₄,

C_2H_3 , C_3H , and C_n ($n=1-3$) by using classical trajectory methods. Acetylene chemisorbs more readily on a terrace than on a ledge structure. all of the radical species investigated have chemisorption rate coefficients in the range 10^{11} to 10^{12} $cm^3/mol\ s$. The least reactive species is CH_3 , and atomic carbon has the largest chemisorption rate of all the species considered. A conclusion of this study is that there is an approximate linear correlation between the rate coefficients and the number of atoms present in the radical. [M. D. Perry and L. M. Raff, J. Phys. Chem. 98, 4375 (1994); 98, 8128 (1994).]

III. Grant Personnel

The personnel supported by this grant and contributed to the research described in this report are:

Principal Investigators:

Professor Lionel M. Raff

Professor Donald L. Thompson

Postdoctoral Research Associates:

Dr. Xiao Yan Chang

Dr. James Peploski

Dr. Paras M. Agrawal

Dr. Dan C. Sorescu

Graduate Students:

Mr. Dan C. Sorescu (Ph.D., 1995)

Undergraduate Students:

Mr. Bruce Spath (B.S., 1993); currently a graduate student at the University of California, Berkeley.